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JC10 Rec'd PCT/PTO 01 MAR 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Atty. Dkt. No: 5045-03200

Inventor(s):

Gidner et al.

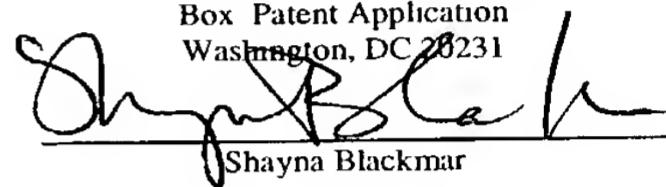
Title: A HIGH PRESSURE AND  
HIGH TEMPERATURE  
REACTION SYSTEM

CERTIFICATE OF EXPRESS MAIL  
UNDER 37 C.F.R. § 1 10

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Washington, DC 20231



Shayna Blackmar

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED  
OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. § 371

INTERNATIONAL APPLICATION NO.: PCT/SE00/01675

INTERNATIONAL FILING DATE: August 31, 2000

PRIORITY DATE CLAIMED: September 3, 1999

U.S. APPLICATION NO. (If known): Unknown

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1.  This is a FIRST submission of items concerning a filing under 35 U.S.C. § 371.
2.  This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. § 371.
3.  This is an express request to begin national examination procedures (35 U.S.C. § 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. § 371(b) and PCT Articles 22 and 39(l).
4.  A translation of the International Application into English (35 U.S.C. § 371(c)(2)), including:  
a title page; \_\_\_\_\_ page specification; \_\_\_\_\_ page(s) of claims (claims \_\_\_\_\_ - \_\_\_\_\_); \_\_\_\_\_ page abstract.
5.  Drawings  
 Formal Figure(s) 1-3 on 2 sheet(s).
6.  A copy of the International Application as filed (35 U.S.C. § 371(c)(2))  
 is transmitted herewith including: a title page; 12 page specification; 6 page(s) of claims (claims 1-32);  
1 page abstract.  
 has been transmitted by the International Bureau.  
 A copy of Form PCT/IB/308 (1 page) is enclosed.  
 is not required, as the application was filed in the United States Receiving Office (RO/US).

7.  A copy of the International Publication, Publication No. WO 01/017915.
8.  Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. § 371(c)(3))
  - are transmitted herewith (required only if not transmitted by the International Bureau).
  - have been transmitted by the International Bureau.
  - have not been made; however, the time limit for making such amendments has NOT expired.
  - have not been made and will not be made.
9.  A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. § 371(c)(3)).
10.  A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
  - A copy of the Demand for International Preliminary Examination is enclosed.
11.  An oath or declaration of the inventor(s) (35 U.S.C. § 371(c)(4)):
  - is enclosed (3 pages).
  - a combined Declaration and Power of Attorney is enclosed (\_\_\_\_ pages).
  - is not enclosed. Applicant requests the Patent and Trademark Office to accept this application and accord a serial number and filing date as of the date this application is deposited with the U.S. Postal Service for Express Mail. Further, Applicant requests that the NOTICE OF MISSING PARTS-FILING DATE GRANTED be sent to the undersigned representative of Applicant.
12.  Applicant hereby claims priority to:
  - International Application No.: PCT/SE00/01675 filed August 31, 2000.
  - Swedish Application No.: SE 9903113-0 filed September 3, 1999.
  - A copy of Form PCT/IB/304 (1 page) indicating receipt of the priority document by the International Bureau is enclosed.
13.  A translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. § 371(c)(5)).
14.  The entire disclosure of the International Application referred to above is considered to be part of the accompanying application and is hereby incorporated by reference herein.
15.  Assignment Papers.
  - An assignment document is enclosed for recording (2 pages).
  - Form PTO-1595 Assignment Recordation Cover Sheet (1 page).
16.  A Preliminary Amendment (7 pages).
17.  A substitute specification for pages \_\_\_\_ (\_\_\_\_ pages).
18.  A strikethrough version of specification and abstract (\_\_\_\_ pages).
19.  Power of Attorney
  - Is enclosed.
  - a combined Declaration and Power of Attorney is enclosed.
20.  Information Disclosure Statement (IDS), including:
  - Form PTO-1449
  - Reference(s) marked according to Form PTO-1449.
21.  Return Receipt Postcard
22.  Small Entity Status
  - A small entity statement is enclosed.

- Small entity status is proper and is requested.
- 23  Copy of International Request.
24.  Copy of International Preliminary Examination Report.  
 A copy of the International Preliminary Examination Report in English.  
 English Translation of the International Preliminary Examination Report.
25.  The following fees are submitted:

<b>BASIC NATIONAL FEE (37 CFR § 1.492 (a) (1)-(5):</b>																		
<input type="checkbox"/> Neither international preliminary examination fee nor international search fee paid to USPTO and International Search Report not prepared by the EPO or JPO.....\$1040.00																		
<input checked="" type="checkbox"/> International preliminary examination fee not paid to USPTO but International Search Report prepared by the EPO or JPO.....\$890.00																		
<input type="checkbox"/> International preliminary examination fee not paid to USPTO but international search fee paid to USPTO.....\$740.00																		
<input type="checkbox"/> International preliminary examination fee paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4).....\$710.00																		
<input type="checkbox"/> International preliminary examination fee paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4).....\$100.00																		
<b>ENTER APPROPRIATE BASIC NATIONAL FEE AMOUNT (as selected above):</b>		<b>\$890.00</b>																
Surcharge of \$130.00 for furnishing oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 Months from the earliest claimed priority date (37 C.F.R. § 1.492(e)).																		
<table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 25%;">CLAIMS</th> <th style="width: 25%;">NUMBER FILED</th> <th style="width: 25%;">NUMBER EXTRA</th> <th style="width: 25%;">RATE</th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>38 - 20 =</td> <td>18</td> <td>x \$18.00 =</td> </tr> <tr> <td>Independent claims</td> <td>2 - 3 =</td> <td>0</td> <td>x \$78.00 =</td> </tr> <tr> <td colspan="3" style="text-align: right;"><b>MULTIPLE DEPENDENT CLAIM(S)</b></td> <td>+ \$260.00 =</td> </tr> </tbody> </table>		CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	Total claims	38 - 20 =	18	x \$18.00 =	Independent claims	2 - 3 =	0	x \$78.00 =	<b>MULTIPLE DEPENDENT CLAIM(S)</b>			+ \$260.00 =	
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<b>MULTIPLE DEPENDENT CLAIM(S)</b>			+ \$260.00 =															
<b>TOTAL OF ABOVE CALCULATIONS:</b>		<b>\$1214.00</b>																
Reduction by 50% for Small Entity. A Small Entity Statement must be filed:																		
<b>SUBTOTAL:</b>		<b>\$607.00</b>																
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 Months from the earliest claimed priority date:																		
<b>TOTAL NATIONAL FEE:</b>		<b>\$607.00</b>																
Fee for recording the enclosed assignment. The assignment must be accompanied by an appropriate cover sheet. \$40.00 per property:		\$40.00																
<b>TOTAL FEES ENCLOSED:</b>		<b>\$647.00</b>																

- A fee authorization in the amount of \$647.00 is enclosed.
- Please charge my Deposit Account No. 50-1505/      in the amount of      to cover the above fees.
- The Commissioner is hereby authorized to charge any other fees which may be required or credit any overpayment to Conley, Rose, & Tayon, P.C., Deposit Account No. 50-1505/5045-03200/EBM.

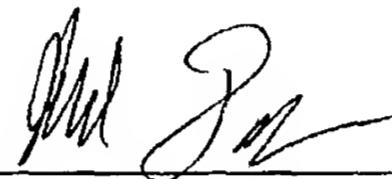
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Date

44,649

3/1/02

**PATENT 5045-03200****IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Application No.: Unknown  
 Filed: Herewith  
 Inventor(s):  
 Gidner et al.

Title: A HIGH PRESSURE AND  
 HIGH TEMPERATURE  
 REACTION SYSTEM

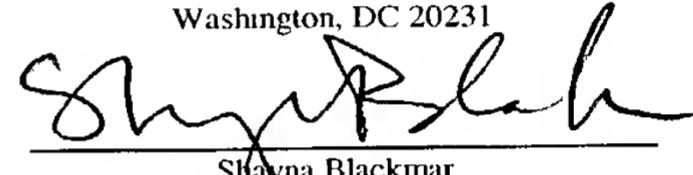
§ Examiner: Unknown  
 § Group/Art Unit: Unknown  
 § Atty. Dkt. No: 5045-03200

**CERTIFICATE OF EXPRESS MAIL  
 UNDER 37 C.F.R. §1.10**

"Express Mail" mailing label number EL893865445US  
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Commissioner for Patents  
 Box Patent Application  
 Washington, DC 20231

  
 Shayna Blackmar

**PRELIMINARY AMENDMENT**

Commissioner for Patents  
 Box Patent Application  
 Washington, DC 20231

Sir:

Please amend the above-captioned application as follows:

***In the Claims:***

Please cancel claims 1-32 without prejudice.

Please add the following claims.

33. (new) A method for oxidative waste treatment, comprising:

injecting a first fluid of a first temperature at a first flow rate into a second fluid of a

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second temperature at a second flow rate, wherein the first fluid is corrosive in a corrosive temperature range, wherein the corrosive temperature range excludes the second temperature and includes the first temperature;

transporting the first fluid in a first conduit adapted to transport the first fluid;

transporting the second fluid in a second conduit adapted to transport the second fluid, wherein the first conduit comprises an end within the interior of the second conduit, and wherein the first conduit is in fluid communication with the second conduit; and

mixing the first and the second fluids in the second conduit within a mixing length downstream of the end of the first conduit, wherein the second conduit comprises a tube or liner having at least an inner surface area made of a corrosion resistant material and extending along the mixing length to inhibit corrosion of the second conduit;

wherein the first and second temperatures and the first and second flow rates are selected such that the mixed fluids downstream of the mixing length are at a temperature that is substantially non-corrosive for the first fluid.

34. (new) The method of claim 33, wherein the corrosive temperature range lies between the first temperature and the second temperature.

35. (new) The method of claim 33, wherein the first fluid is corrosive at the first temperature, and wherein at least an inner surface area of the first conduit is made of a corrosion resistant material to inhibit corrosion of the first conduit.

36. (new) The method of claim 33, wherein the first fluid comprises nitric acid, and wherein the corrosive temperature range is between about 270 °C and about 380 °C.

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37. (new) The method of claim 33, wherein the first fluid comprises sulfuric acid.
38. (new) The method of claim 33, wherein the first fluid comprises hydrochloric acid.
39. (new) The method of claim 33, wherein the first fluid comprises a halogen.
40. (new) The method of claim 33, wherein the second temperature is selected to be higher than the corrosive temperature range, and wherein the first and second temperatures and the first and second flow rates are selected such that the temperature of the mixed fluids downstream of the mixing length is higher than the corrosive temperature range.
41. (new) The method of claim 40, wherein the second fluid comprises supercritical water.
42. (new) The method of claim 41, wherein the second fluid comprises nitrogenous compound.
43. (new) The method of claim 33, further comprising feeding the mixed fluids from the second conduit to a reactor of a high pressure and high temperature reaction system for oxidation of waste material.
44. (new) The method of claim 33, wherein the second conduit comprises part of a reactor of a high pressure and high temperature reaction system for oxidation of waste material.
45. (new) The method of claim 33, wherein the second temperature is selected to be lower than the corrosive temperature range, and wherein the first and second temperatures and the first and second flow rates are selected such that the temperature of the mixed fluids downstream of the mixing length is lower than the corrosive temperature range.

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46. (new) The method of claim 45, wherein the second fluid comprises cooling water.
47. (new) The method of claim 46, wherein the first fluid comprises destructed supercritical wastewater output from a reactor of a high pressure and high temperature reaction system.
48. (new) The method of claim 47, wherein the mixed fluids in the second conduit are output from the high pressure and high temperature reaction system.
49. (new) The method of claim 33, wherein at least the inner surface area of the tube or liner is made of a material selected from the group of titanium, zirconium, platinum, tantalum, niobium, or alloys thereof.
50. (new) A high pressure and high temperature reaction system suitable for oxidative waste treatment, comprising:
  - a first conduit adapted to transport a first fluid of a first temperature at a first flow rate;
  - a second conduit adapted to transport a second fluid of a second temperature at a second flow rate, wherein the first fluid is corrosive in a corrosive temperature range, and wherein the corrosive temperature range excludes the second temperature and includes the first temperature;
  - wherein the first conduit comprises an end within the interior of the second conduit, wherein the first conduit is in fluid communication with the second conduit such that the first fluid and the second fluid can be mixed in the second conduit within a mixing length from the end of the first conduit, and wherein a temperature of the mixed fluids downstream of the mixing length is substantially non-corrosive for the first fluid; and
  - a tube or liner comprising at least an inner surface area made of a corrosion resistant

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material, wherein the tube or liner comprises part of the second conduit and extends along the mixing length to inhibit corrosion of the second conduit, wherein the second conduit comprises a conventional construction material upstream and downstream of the tube or liner, wherein the conventional construction material is configured for high pressure and high temperature reaction systems suitable for supercritical water oxidation, and wherein the second conduit comprises a nickel based alloy.

51. (new) The system of claim 50, wherein the corrosive temperature range lies between the first temperature and the second temperature.

52. (new) The system of claim 50, wherein the first conduit is adapted to transport the first fluid which is corrosive at the first temperature, and wherein at least an inner surface area of the first conduit comprises a corrosion resistant material to inhibit corrosion of the first conduit.

53. (new) The system of claim 50, wherein the first fluid comprises nitric acid, and wherein the corrosive temperature range is between about 270 °C and about 380 °C.

54. (new) The system of claim 50, wherein the first fluid comprises sulfuric acid.

55. (new) The system of claim 50, wherein the first fluid comprises hydrochloric acid.

56. (new) The system of claim 50, wherein the first fluid comprises a halogen.

57. (new) The system of claim 50, wherein the second conduit is adapted to transport the second fluid at the second temperature which is higher than the corrosive temperature range, wherein the second conduit is adapted to transport the mixed fluids, and wherein the mixed fluids are at a temperature higher than the corrosive temperature range.

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58. (new) The system of claim 57, wherein the second fluid comprises supercritical water.
59. (new) The system of claim 58, wherein the second fluid comprises nitrogenous compound.
60. (new) The system of claim 50, further comprising a reactor for oxidation of waste material, wherein the second conduit is adapted to feed the mixed fluids to the reactor.
61. (new) The system of claim 50, further comprising a reactor for oxidation of waste material, wherein the second conduit comprises part of the reactor.
62. (new) The system of claim 50, wherein the second conduit is adapted to transport the second fluid at the second temperature which is lower than the corrosive temperature range, wherein the second conduit is adapted to transport the mixed fluids, and wherein the mixed fluids are at a temperature lower than the corrosive temperature range.
63. (new) The system of claim 62, wherein the second fluid comprises cooling water.
64. (new) The system of claim 63, further comprising a reactor, wherein the first conduit is adapted to transport the first fluid, and wherein the first fluid comprises supercritical or subcritical wastewater output from the reactor.
65. (new) The system of claim 50, further comprising a high pressure and high temperature reaction system output, wherein the second conduit is adapted to transport the mixed fluids to the system output.
66. (new) The system of claim 50, wherein at least the inner surface of the tube or liner comprises a material selected from the group of titanium, zirconium, platinum, tantalum, niobium, and alloys thereof.

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67. (new) The system of claim 50, wherein the tube or liner is removably arranged in the second conduit.

68. (new) The system of claim 50, wherein the tube or liner extends a predetermined distance upstream of the end of the first conduit.

69. (new) The system of claim 50, wherein the second conduit comprises means for holding and/or positioning the tube or liner in the second conduit.

70. (new) The system of claim 69, wherein the second conduit comprises an elbow at the downstream end of the mixing length, wherein the elbow inhibits the tube or liner from moving along an inner surface of the second conduit in the downstream direction.

It is believed that no fees are due in connection with the filing of this Preliminary Amendment. However, if any fees are due, the Commissioner is hereby authorized to deduct said fees from Conley, Rose & Tayon Deposit Account No. 50-1505/5045-03200/EBM.

Respectfully submitted,



Mark R. DeLuca  
Reg. No. 44,649  
Patent Agent

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Date: 3/1/02

*2/P&gt;***TECHNICAL FIELD OF THE INVENTION**

The present invention generally relates to an apparatus for mitigation of corrosion  
5 in a high pressure and high temperature reaction system, specifically in a system suitable  
for oxidative waste treatment under supercritical water conditions. The invention relates  
further to the reaction system itself and to a method in said reaction system.

**DESCRIPTION OF RELATED ART AND BACKGROUND OF THE  
10 INVENTION**

Several approaches for disposing of waste are available today, of which the major  
ones are landfilling and incineration. In recent years, another technique based on  
supercritical water oxidation (SCWO) has been commercialized, see, e.g. Supercritical  
15 *Water Oxidation Aims for Wastewater Cleanup*, C.M. Caruana, Chem. Eng. Prog., April  
1995.

Supercritical water oxidation is a novel and advanced process for, inter alia,  
effective destruction of toxic substances, particularly organic pollutions, in wastewater  
20 and sludge. The process converts, fast and effectively, organic materials containing  
substantially carbon and hydrogen to carbon dioxide and water, at a temperature above  
the critical point of water (374°C and 22,13 MPa), while releasing energy. The process  
may be completely contained and the destruction efficiency is often higher than 99%.

25 Heavy metals present during the process are converted to their oxides whereas  
sulfur and phosphorous are converted to sulfate and phosphate, respectively. Halogens  
are converted to their corresponding acids, e.g., hydrochloric acid. Smaller amounts of  
nitrogen compounds, e.g. amines and ammonia, which exist in the waste material flow,  
are converted to molecular nitrogen, and not to NO<sub>x</sub>, which is an acidifying and  
30 fertilizing residual product and therefore undesirable in the effluent.

If, however, the waste material contains large amounts of ammonia and/or organic nitrogen compounds, substantial amounts of the nitrogen source may be found in the effluent as ammonia as a result of the destruction process. This phenomenon is undesirable as ammonia constitutes a fertilizing compound. Besides, discharge of 5 ammonia without further purifying is very often imposed with restrictions.

It is known in the literature, e.g. through *Reactions of Nitrate Salts with Ammonia in Supercritical Water*, P.C. Dell'Orco et al., Ind. Eng. Chem., Vol. 36, No. 7, 1997, and references therein, that ammonia can be converted to molecular nitrogen during 10 supercritical water oxidation conditions if nitric acid is used as a co-oxidant together with molecular oxygen, hydrogen peroxide or another suitable compound. The nitric acid has preferably to be supplied to the waste material flow firstly after that the organic contents have been destructed with oxygen as nitrate otherwise will compete with oxygen in the destruction of the organic contents. Furthermore, the nitric acid has to be dosed with 15 high accuracy relative to the amount of ammonia (a stoichiometric amount is needed). If too little nitric acid is supplied, a remaining amount of ammonia will be left whereas too large amounts of nitric acid will result in an excess of nitrate in the effluent.

For purposes of strength and corrosion, nickel-based alloys, such as Hastelloy or 20 Inconel, are employed for manufacturing of equipment for SCWO. Acids, and not at least nitric acid, are, however, in presence of oxygen strongly corrosive at high temperatures, though still subcritical ones, even if these corrosion resistant nickel alloys are used, see, e.g. *The Corrosion of Nickel-base Alloy 625 in Sub- and Supercritical Aqueous Solutions of HNO<sub>3</sub> in the Presence of Oxygen*, P. Kritzer et al., J. Mater. Sci. 25 Lett., 1999, in print, and references therein. It was found in the temperature-resolved corrosion measurements reported that the corrosion due to nitric acid was most severe at temperatures between about 270°C and 380°C, the same temperature range in which general corrosion is caused by the mixtures HCl/O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>/O<sub>2</sub>, respectively. At supercritical temperatures the corrosion rates were low.

30

For this reason, particular solutions must be employed for the entry of nitric acid into the supercritical wastewater flow containing ammonia or ammonium salts to avoid or at least minimize the corrosion.

5        However, as regards corrosion, generally the most troublesome compound in the supercritical water oxidation process is the chlorine element, since it is very common in various chemical substances. If the chlorine is present as an ion at elevated temperatures, it will corrode the construction materials mentioned above. The chlorine may have been an ion originally, liberated during heat up or in the reactor.

10

US 5,358,645 issued to Hong et al. disclose an apparatus and process for high temperature water oxidation, the apparatus (not in detail described) having a surface area, that may be exposed to corrosive material, composed of zirconia based ceramics. The ceramics may be employed as coatings or linings.

15

US 5,461,648 issued to Nauflett et al. disclose a supercritical water oxidation reactor with a corrosion-resistant lining. The inner surface of the reactor vessel is coated with artificial ceramic or diamond. A cylindrical baffle for introducing the oxygenating agent extends axially within the interior of the vessel and has its exterior surface inside 20 the vessel coated with said artificial ceramic or diamond.

US 5,552,039 issued to McBrayer, Jr. et al. disclose a turbulent flow cold-wall reactor. It mentions, inter alia, that if the atmosphere in the reaction chamber is harsh and corrosive, the inside wall of the reaction chamber should preferably be made of or 25 covered with a coating or a liner withstanding the harsh atmosphere.

None of these US patents, is, however, discussing corrosion problems in terms of temperature dependent corrosivity, or the particular corrosion caused by the corrosive compounds discussed above.

30

**SUMMARY OF THE INVENTION**

It is consequently an object of the present invention to provide an apparatus for use in a high pressure and high temperature reaction system, specifically in a system  
5 suitable for oxidative waste treatment under supercritical water conditions, that mitigates or eliminates the occurrence of corrosion.

It is a further object of the invention to provide such an apparatus that is effective, robust, and easy to install and of low cost.

10

It is yet a further object of the invention to provide the apparatus in such a way that it is easily replaceable in the reaction system.

15

These objects among others are, according to one aspect of the invention, attained by an apparatus as claimed in Claim 1.

A further object of the present invention is to provide a method for disposing of waste using said apparatus.

20

Consequently, there is according to a second aspect of the present invention provided a method as claimed in Claim 22.

25

An advantage of the present invention is that it allows the main parts of the reaction system, including the reactor itself, to be constructed of a relatively inexpensive material such as nickel based and nickel-chromium alloys, and still use or be able to treat corrosive materials in the process.

**BRIEF DESCRIPTION OF THE DRAWINGS**

30

The present invention will become more fully understood from the detailed description of embodiments of the present invention given hereinbelow and the

accompanying Figs. 1-3 which are given by way of illustration only, and thus are not limitative of the invention.

Fig. 1 shows a simplified block diagram of a reaction system suitable for  
5 oxidative waste treatment under supercritical water conditions wherein the present  
invention may be employed.

Fig. 2 shows, in cross-section, a first embodiment of an apparatus according to the  
present invention.

10

Fig. 3 shows, in cross-section, a second embodiment of an apparatus according to  
the present invention.

## DETAILED DESCRIPTION OF EMBODIMENTS

15

In the following description, for purposes of explanation and not limitation,  
specific details are set forth, such as particular hardware, applications, techniques, etc.  
in order to provide a thorough understanding of the present invention. However, it will  
be apparent to one skilled in the art that the present invention may be practiced in other  
20 embodiments that depart from these specific details. In other instances, detailed  
descriptions of well-known methods, protocols, apparatus, and circuits are omitted so as  
not to obscure the description of the present invention with unnecessary details.

Considering Fig. 1, the operation of a high pressure and high temperature  
25 reaction system 10 such as a system suitable for oxidative waste treatment under  
supercritical water conditions, will briefly be overviewed so that in the subsequent  
detailed description of the present invention, the operation of the inventive apparatus may  
be better understood.

30 A conventional reaction system 10 comprises a primary tank 12, a heat exchanger  
14, a heater 16 and a reaction chamber 18. A primary wastewater stream 20 passes

initially through the first compartment (not shown) of the heat exchanger 14, then through the heater 16, and enters the reaction chamber 18 under pressure, after it has been mixed with oxidant coming through feed line 22. The organic matter contained in the primary waste stream 20 is oxidized, and in sequence, the hot effluence passes through 5 the second compartment (not shown) of the heat exchanger 14. As well known, heat exchangers usually have two compartments, physically isolated from each other, which, however, are heat-communicating. The second compartment transfers heat to the first compartment.

10           Constructing materials for the reactor and the tubing may comprise steel, nickel-based alloys, platinum, gold, titanium, zirconium, ceramics, ceramic composites and other corrosion resistant materials as the environment inside the reaction chamber and tubing may be hostile and corrosive. However, as many of the latter materials are highly expensive, an optimal compromise between cost, on one hand, and corrosion resistance, 15 on the other hand, is to use nickel based alloys such as Hastelloy or Inconel, for the manufacturing of such equipment.

As already discussed in the prior art, there is a number of species that are very aggressive relative to these nickel based alloys within a finite temperature range, among 20 them nitric acid, sulfuric acid and hydrochloric acid. All these three acids are strongly corrosive between about 270 and 380°C, but the corrosion rates for the latter two acids are lower by a factor of ten than the one found for nitric acid, see said Kritzer article.

It is clear from the description above of the operation of the system that the 25 wastewater flow, as well as any additives, will be heated from initial low temperatures, which probably are close to ambient temperatures, up to supercritical temperatures (above 374°C) for the oxidative treatment of the waste, whereafter the effluent is cooled either in a heat exchanger or by mixing it with quench water or a combination of both.

30           The present inventors have realized that if the initial temperatures and the temperature of the cooled effluent are kept preferably well below 270°C and the

temperature in the reaction chamber is kept preferably above 380°C, there is generally only two sections of a reaction system made of nickel-based alloy that may be attacked by corrosive agents such as those mentioned above contained in, or supplied to, the wastewater flow, namely a "heating" section and a "cooling" section, where the 5 temperatures are within the temperature interval of said corrosion.

The present invention is thus concerned with such sections of the reaction system and how to design them in order to provide a reaction system of low cost and good 10 corrosion resistance. The idea is to provide appropriate tubing (made of nickel based alloy or other, preferably relatively inexpensive, material that is not corrosive resistant) of the system with a corrosive resistant tube or liner. The number of tubes or liners, their positions and their lengths are chosen in order to protect the system from corroding.

Hereinbelow will follow a few implementation examples of the present invention. 15 Note that the terms "corrosive" and "corrosive-resistant material" as used in the description below and in the appended claims should be understood as "corrosive" relative conventional construction material for high pressure and high temperature reaction systems suitable for supercritical water oxidation such as steel, nickel based alloys, nickel-chromium alloys and the like, at least within a given temperature interval, 20 and "corrosive-resistant material" refers to unconventional expensive material which is corrosion-resistant relative a wide variety of harsh media such as acids, particularly the acids discussed above, halogens and the like, respectively. Examples of corrosion-resistant materials will be given below.

25 A first embodiment of the present invention, shown in Fig. 2, depicts an apparatus 101 for introducing nitric acid in a supercritical water flow containing ammonia or ammonium with the purpose of converting this to molecular nitrogen.

In a section of a reaction system tube 103, which preferably is the conduit 30 between the heater 16 and the reaction chamber 18, or part of the reaction chamber itself, of Fig. 1, a separate tube or liner 105 of a corrosion resistant material is mounted, the

outer surface of which is in fit with the inner surface of reaction system tube 103.

Alternatively, tube 105 constitutes part of the reaction system tube 103 itself (not shown).

A feeding pipe 107 of relatively small diameter, is mounted through an opening of  
5 tube 103 and extends substantially axially with tube 103 and liner 105, and which ends in  
the interior of tube 103. Preferably, feeding pipe 107 and tube 103 are concentrically  
arranged for transportation of fluids, the former nitric acid and the latter preheated  
wastewater feed, in the same directions, as indicated by arrows 109-113. The  
temperature of the wastewater should preferably be above 380°C, and the temperature of  
10 the nitric acid should be low, preferably considerably lower than 270°C. Note that if the  
concentration of the corrosive agent is low, these temperature limits are not very crucial,  
i.e., the corrosion would be low at temperatures slightly lower than 380°C and,  
particularly, at temperatures slightly higher than 270°C, e.g., 300°C.

15 By pumping nitric acid through the feeding pipe it will be preheated by the hot  
water flow and then get mixed with the supercritical water. The flow rates are such that  
the total flow (wastewater and nitric acid) becomes supercritical with a temperature of  
above 380°C after having reached a steady temperature state a certain distance 115 from  
the end of the feeding pipe, said distance being referred to as the heat transfer or mixing  
20 length. Accordingly, to avoid any risk of corrosion of the inner walls of tube 103, the  
length of the liner 105 should be of at least this length, and it should be localized to  
protect the inner walls of tube 103 within this length. For practical reasons, the liner 105  
may have an offset 117 in the end facing the end of the feeding pipe, i.e. extend beyond  
(upstream of) said feeding pipe end to avoid any risk of corrosion in that region.

25

The material of the liner and preferably of the feeding pipe is chosen according to  
its corrosion resistance relative nitric acid at the occurring temperatures. Literature data  
shows that titanium, generally, is a suitable material, but also materials such as  
zirconium, platinum, tantalum, niobium and ceramics may be chosen. The entire liner, or  
30 an inner coating thereof, may be constructed of such material.

Even if a limited degree of corrosion may exist using these materials, the components are relatively cheap and easy to replace when so needed.

Preferably, there are means for positioning and/or holding the liner in place. In  
5 the embodiment showed, tube 103 is provided with an elbow at the downstream end of the mixing length to prevent liner 105 from moving further downstream. However, any suitable means for positioning and/or holding the liner, e.g. flanges at the inner walls of tube 103, may be used.

10 In experimental work, an injection apparatus as the one shown in Fig. 2, was used, the liner and the feeding pipe being made of titanium. The ammonia destruction was performed by pumping 65% nitric acid into the reaction system during several hours without any detected corrosion. When the liner and the feeding pipe were demounted and inspected no corrosion of these components was discovered. In contrast thereto, in  
15 an experiment in which nitric acid was pumped into a supercritical water flow containing ammonia through a T-pipe of Inconel 625, the pipe was destroyed through corrosion in just a few hours.

Consequently, by using an injection apparatus according to Fig. 2, nitric acid may  
20 safely be introduced without severe corrosion of the reaction system.

Furthermore, a substantial portion of the reaction between nitric acid and ammonia and/or ammonium will take part as early as in the section of the reaction system where the liner is localized, which further reduces the risk for severe corrosion.

25 Alternatively, feeding pipe 107 and tube 103 of Fig. 2 may be arranged for transportation of a wastewater feed containing a corrosive agent such as a halogen, and water or a wastewater feed in lack of such a corrosive agent, respectively. The water or wastewater in tube 103 is preferably at a supercritical temperature, whereas the corrosive  
30 wastewater may be cooler.

Referring next to Fig. 3, which illustrates an apparatus 201 according to a second embodiment of the present invention, a separate tube or liner 205 of a corrosion resistant material is mounted in a section of a reaction system tube 203, which is preferably at the effluent output or elsewhere in the exit path tubing. The outer surface of liner 205 is  
5 arranged to be in fit with the inner surface of the reaction system tube 203.

A first input tube 207, is mounted through an opening of tube 203 and extends substantially axially, preferably concentrically, with tube 203 and liner 205, and which ends in the interior of tube 203. A second input tube 208 is connected to tube 203  
10 upstream from said end of input tube 207.

Input tube 207 and input tube 208 are arranged for transporting effluent from reactor 18 containing corrosive compounds such as nitric acid, sulfur acid, or the like, and quench water, respectively, in the directions as indicated by arrows 209-213. The  
15 effluent stream is supercritical or close to supercritical, and the temperature of the quench water is low, preferably at ambient temperature.

By pumping appropriate amounts of quench water through input tube 208, the effluent input through tube 207 will be cooled effectively by the quench water and get  
20 mixed with it. The flow rates are such that the total flow (effluent and quench water) will have a temperature of below a certain temperature, e.g. 270°C, depending on concentration of corrosive compounds, after having reached a steady temperature state a certain distance 215 from the end of the input tube 207, said distance being referred to as the mixing length. Accordingly, to avoid any risk of corrosion of the inner walls of tube  
25 203, the length of the liner 205 should be at least of this mixing length, and it should be localized to protect the inner walls of tube 203 within this length. For practical reasons, the liner 203 may have an offset 217 in the end facing the end of tube 207, i.e. extend beyond (upstream of) said tube end, to avoid any risk of corrosion in that region.

30 The material of the liner and preferably of tube 207, as well as suitable means for positioning and/or holding the liner in place may be chosen as in the first embodiment.

The first and the second embodiments of the present invention may be modified to include a heat exchange for assisting in increasing or decreasing the temperature in 5 tubes 103 and 203, respectively. Hereby, the lengths of liners 105 and 205, respectively, may be shortened.

As a further example of an implementation of the present invention (not illustrated in the drawings), an effluent from the reactor containing chlorine ions is pre-cooled in a heat exchanger by part of the incoming waste stream, to a temperature well above 380°C, e.g., 400°C. The effluent is then cooled by an apparatus according to the 10 present invention to a sufficient low temperature, e.g., 260°C, to minimize corrosion. After leaving the apparatus, the effluent water mixture is further cooled by the remaining 15 of the waste stream.

15

It will be obvious that the invention may be varied in a plurality of ways. For instance, the geometry and function of the reaction system and the appearance of the tubing may deviate substantially from the description above. Such and other variations 20 are not to be regarded as a departure from the scope of the invention. All such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the appended claims.

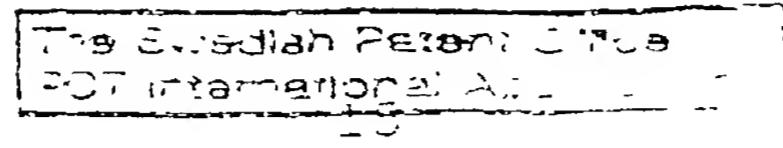
CLAIMS

1. In a high pressure and high temperature reaction system suitable for oxidative waste treatment, particularly a reaction system for supercritical water oxidation (SCWO), a method for 5 injecting a first fluid of a first temperature at a first flow rate into a second fluid of a second temperature at a second flow rate, said first fluid being corrosive only in a temperature range which excludes said second temperature and includes said first temperature or which lies between said first 10 and second temperatures, characterized by

- transporting the first fluid in a first conduit (107, 207) adapted therefore;
- transporting the second fluid in a second conduit (103, 203) adapted therefore, wherein said first conduit (107, 207) ends in 15 the interior of said second conduit (103, 203), and thus communicates with said second conduit; and
- mixing the first and the second fluids (115, 215) in said second conduit within a mixing length downstream of said first conduit end, wherein said second conduit is provided with a tube or liner (105, 205) having at least its inner surface area made 20 of a corrosion resistant material, and extending along said mixing length (115, 215) to protect said second conduit (103, 203) from corroding; wherein
- the first and second temperatures and the first and second flow rates are selected such that a temperature of the mixed fluids downstream of said mixing length (115, 215) is obtained, 25 at which said first fluid being substantially non-corrosive.

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2. The method as claimed in Claim 1, wherein said first fluid is corrosive at said selected first temperature and wherein at least the inner surface area of said first conduit (107, 207) is made of a corrosion resistant material to protect said first conduit (107, 207) from corroding.
- 5
3. The method as claimed in Claim 1 or 2, wherein said first fluid contains nitric acid and said corrosive temperature range at which said first fluid is corrosive ranges between about 270°C and 380°C.
- 10 4. The method as claimed in any of Claims 1-3, wherein said first fluid contains sulfuric acid and/or hydrochloric acid and/or any halogen.
5. The method as claimed in any of Claims 1-4, wherein said second temperature is selected to be higher than said 15 temperature range at which said first fluid is corrosive, and wherein the first and second temperatures and the first and second flow rates are selected such that said temperature of the mixed fluids downstream of said mixing length is higher than said temperature range at which said first fluid is corrosive.
- 20 6. The method as claimed in Claim 5, wherein said second fluid contains supercritical wastewater.
7. The method as claimed in Claim 6, wherein said second fluid contains nitrogenous compound.
8. The method as claimed in any of Claims 3-7, comprising 25 feeding the mixed fluids in said second conduit (103, 203) to a reactor (18) of the high pressure and high temperature reaction system (10) for oxidation of waste material.

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9. The method as claimed in any of Claims 3-7, wherein said second conduit (103, 203) is part of a reactor (18) of the high pressure and high temperature reaction system, wherein waste material is oxidized.
10. The method as claimed in any of Claims 1-4, wherein said second temperature is selected to be lower than said temperature range at which said first fluid is corrosive, and wherein the first and second temperatures and the first and second flow rates are selected such that said temperature of the mixed fluids downstream of said mixing length is lower than said temperature range at which said first fluid is corrosive.
11. The method as claimed in Claim 10, wherein said second fluid contains cooling water.
12. The method as claimed in Claim 11, wherein said first fluid contains destructed supercritical wastewater output from a reactor (18) of the high pressure and high temperature reaction system (10).
13. The method as claimed in Claim 12, wherein the mixed fluids in said second conduit (103, 203) are output from the high pressure and high temperature reaction system (10).
14. The method as claimed in any of Claims 1-13, wherein said at least inner surface area of the tube or liner (105, 205) is made of a material selected from the group of titanium, zirconium, platinum, tantalum, niobium and alloys thereof.
15. A high pressure and high temperature reaction system suitable for oxidative waste treatment, particularly a reaction system for supercritical water oxidation (SCWO), characterized in

- a first conduit (107, 207) adapted to transport a first fluid of a first temperature at a first flow rate;
  - a second conduit (103, 203) adapted to transport a second fluid of a second temperature at a second flow rate, said first fluid being corrosive in a temperature range which excludes said second temperature and includes said first temperature or which lies between said first and second temperatures;
  - said first conduit (107, 207) ending inside said second conduit (103, 203), and thus communicates with said second conduit, such that the first and the second fluids can be mixed in said second conduit (103, 203) within a mixing length (115, 215) from the end of said first conduit and downstream such that a temperature of the mixed fluids downstream of said mixing length (115, 215) is obtained, at which said first fluid is substantially non-corrosive; and
  - a tube or liner (105, 205) with at least its inner surface area made of a corrosion resistant material, said tube or liner being located in, or constituting part of, said second conduit and extending along said mixing length (115, 215) to protect said second conduit from corroding, and, upstream and downstream of said tube or liner, said second conduit being made of a conventional construction material for high pressure and high temperature reaction systems suitable for supercritical water oxidation, such as a nickel based alloy.
- 25 16. The reaction system as claimed in Claim 15, wherein said first conduit is adapted to transport a first fluid, which is corrosive at said selected first temperature, and wherein at least the inner surface area of said first conduit (107, 207) is made of a corrosion resistant material to protect said first conduit (107, 207) from corroding.

17. The reaction system as claimed in Claim 15 or 16, wherein said first fluid contains nitric acid and said corrosive temperature range at which said first fluid is corrosive ranges between about 270°C and 380°C.

5 18. The reaction system as claimed in any of Claims 15-17, wherein said first fluid contains sulfuric acid and/or hydrochloric acid and/or any halogen.

10 19. The reaction system as claimed in any of Claims 15-18, wherein said second conduit is adapted to transport a second fluid at a second temperature, which is higher than said temperature range at which said first fluid is corrosive, and to transport the mixed fluids, said mixed fluids being of a temperature downstream of said mixing length, which is also higher than said temperature range at which said first fluid is 15 corrosive.

20. The reaction system as claimed in Claim 19, wherein said second fluid contains supercritical wastewater.

21. The reaction system as claimed in Claim 20, wherein said second fluid contains nitrogenous compound.

20 22. The reaction system as claimed in any of Claims 17-21, further comprising a reactor (18) for oxidation of waste material, wherein said second conduit is adapted to feeding the mixed fluids to said reactor.

25 23. The reaction system as claimed in any of Claims 17-21, comprising a reactor (18) for oxidation of waste material, wherein said second conduit (103, 203) is part of said reactor.

24. The reaction system as claimed in any of Claims 15-18, wherein said second conduit is adapted to transport a second

fluid at a second temperature, which is lower than said temperature range at which said first fluid is corrosive, and wherein said second conduit is adapted to transport the mixed fluids, said mixed fluids being of a temperature downstream of said mixing length, which is lower than said temperature range at which said first fluid is corrosive

5 25. The reaction system as claimed in Claim 24, wherein said second fluid contains cooling water.

10 26. The reaction system as claimed in Claim 25, comprising a reactor (18), wherein said first conduit is adapted to transport a first fluid, which contains destructed supercritical or subcritical wastewater output from said reactor.

15 27. The reaction system as claimed in Claim 13, comprising a high pressure and high temperature reaction system output, wherein said second conduit is adapted to transport said mixed fluids to said system output.

20 28. The reaction system as claimed in any of Claims 15-27, wherein said at least inner surface area of the tube or liner (105, 205) is made of a material selected from the group of titanium, zirconium, platinum, tantalum, niobium and alloys thereof.

25 29. The reaction system as claimed in any of Claims 15-28, wherein the tube or liner (105, 205) is removably arranged in said second conduit.

30. The reaction system as claimed in any of Claims 15-29, wherein said tube or liner (105, 205) is extending a predetermined distance (117, 217) upstream of said first conduit end.

31. The reaction system as claimed in any of Claims 15-30, wherein said second conduit is provided with means for holding and/or positioning the tube or liner (105, 205) in said second conduit (103, 203).

5 32. The reaction system as claimed in Claim 31, wherein said second conduit (103, 203) is provided with an elbow (119, 219) at the downstream end of the mixing length (115, 215) in order to prevent said tube or liner (105, 205) from moving along the inner surface of said second conduit (103, 203) in the  
10 downstream direction.

## ABSTRACT

In a high pressure and high temperature reaction system suitable for oxidative waste treatment, particularly a reaction system for supercritical water oxidation (SCWO),

- 5 a method is disclosed for injecting a first fluid of a first temperature at a first flow rate into a second fluid of a second temperature at a second flow rate, mixing the first and the second fluids within a mixing length (115, 215), and wherein the first and second temperatures and the first and second flow rates are selected such that a temperature of the mixed fluids downstream of said mixing length (115, 215) is obtained, at which said
- 10 first fluid being substantially non-corrosive.

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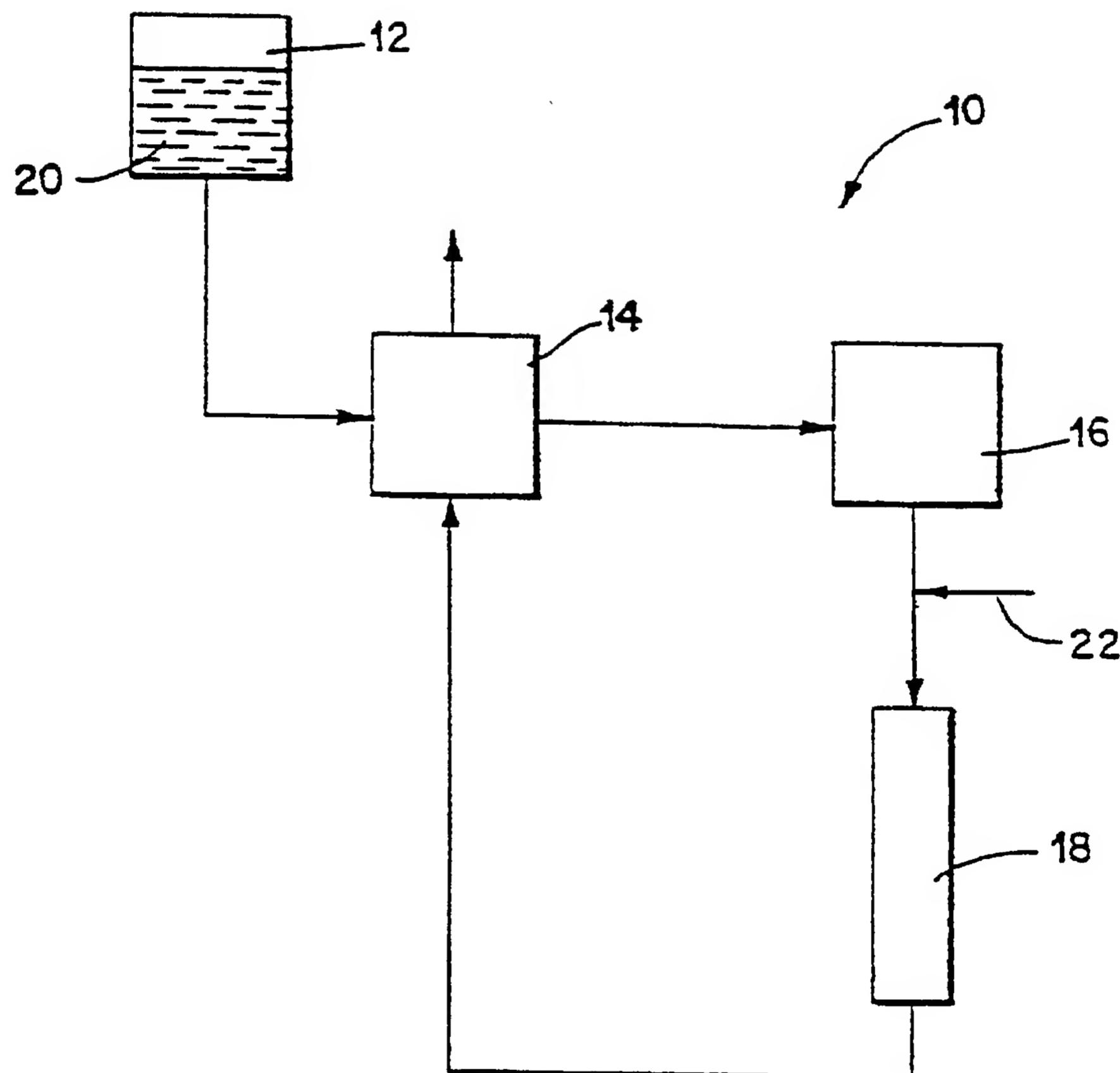


Fig. 1

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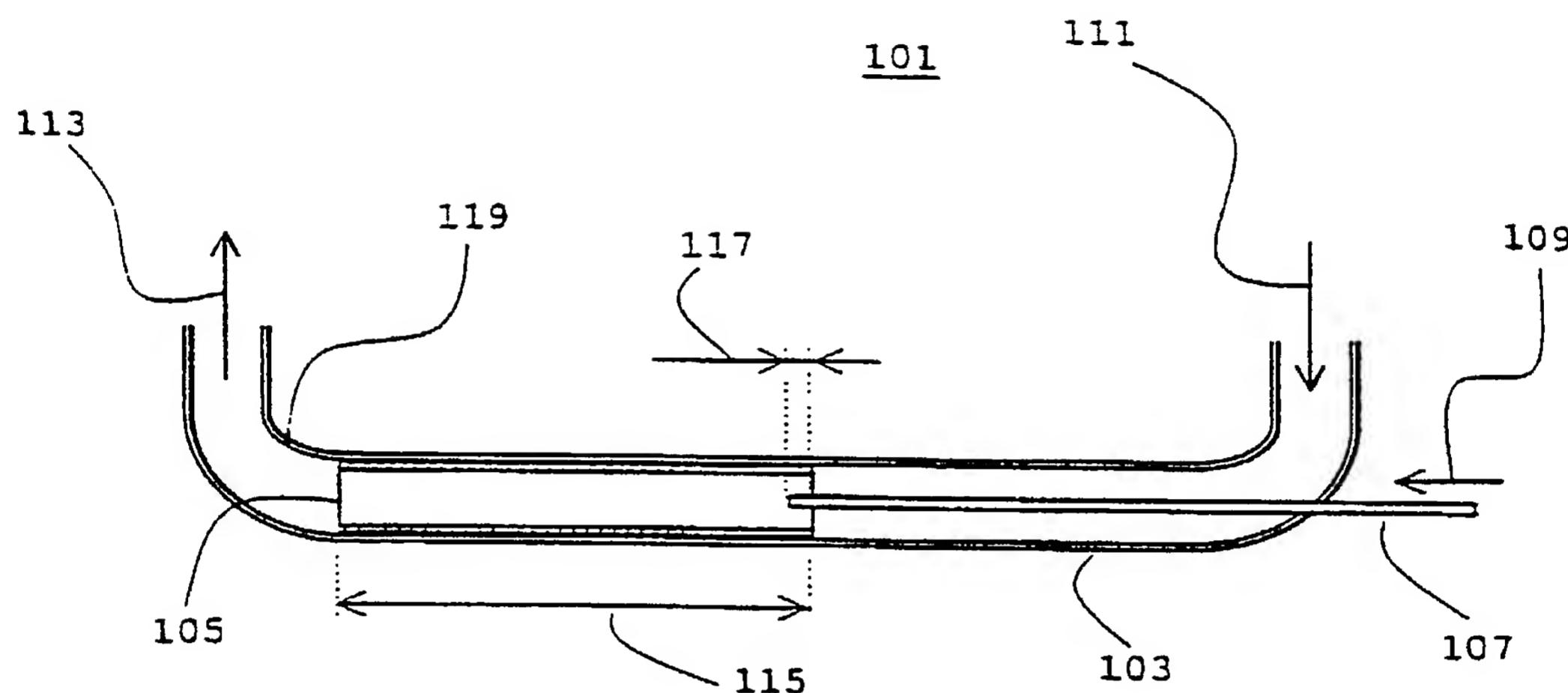


Fig. 2

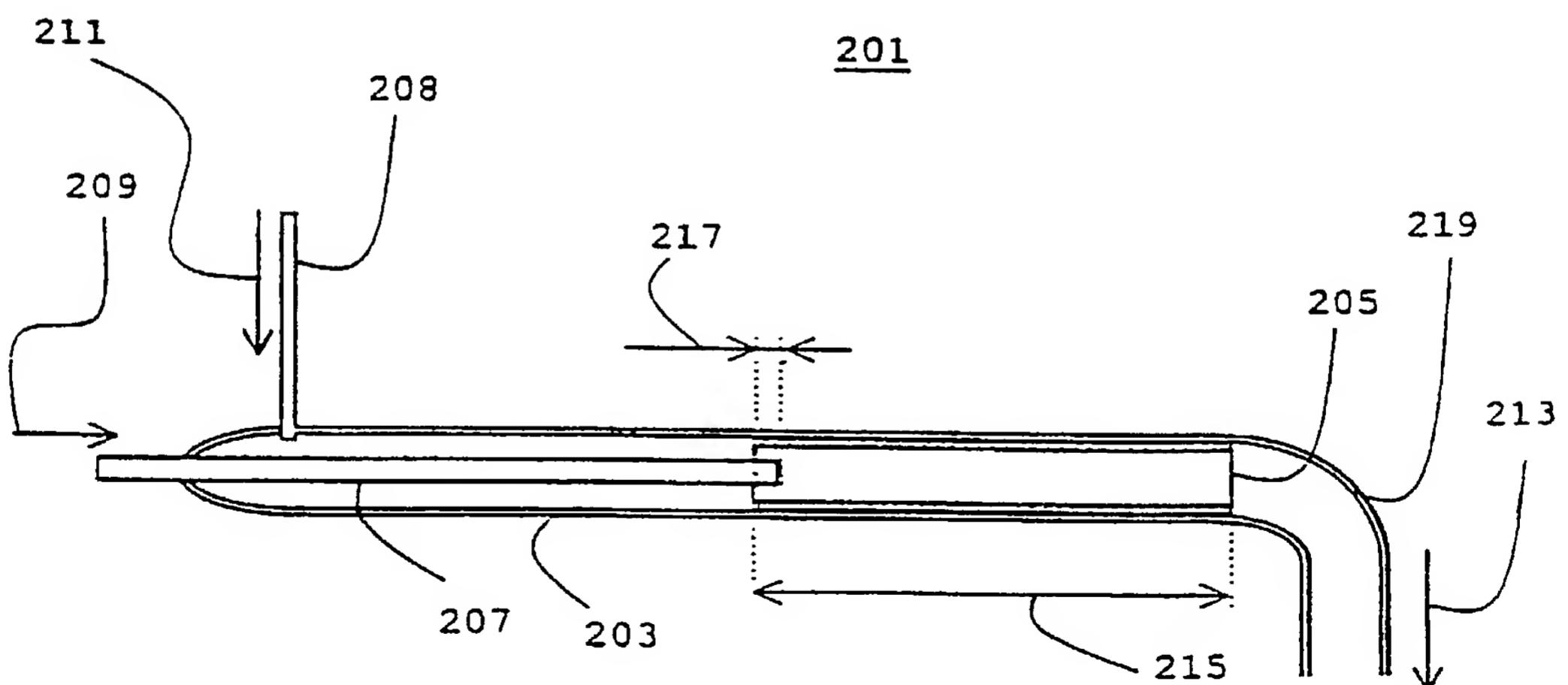


Fig. 3

## PATENT

DECLARATION

As a below named inventor, I hereby declare that:

My residence, post office and citizenship are as stated below next to my name

I believe I am the original, first and sole inventor (if only one name is listed below) or the below named inventors believe they are the original, first and joint inventors (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **A HIGH PRESSURE AND HIGH TEMPERATURE REACTION SYSTEM**, the specification of which:

is attached herewith.  
 was filed on \_\_\_\_\_ as Application Serial No. \_\_\_\_\_.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability of the subject matter claimed in this application, as "materiality" is defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

## PRIOR FOREIGN APPLICATION(S)

			<u>Priority Claimed</u>
9903113-0 (Number)	Sweden (Country)	September 3, 1999 (Date Filed)	Yes
N/A (Number)	(Country)	(Date Filed)	Yes/No

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose all information known to me to be material to the patentability of the subject matter claimed in this application, as "materiality" is defined in Title 37, Code of Federal Regulations, § 1.56, which become available between the filing date of the prior application and the national or PCT international filing date of this application:

N/A (Application Serial No.)	(Filing Date)	Pending (Status)
N/A (Application Serial No.)	(Filing Date)	Pending (Status)

I hereby claim the benefit under title 35, United States code §119(e) of any United States provisional application(s) listed below:

N/A (Application Serial No.)	(Filing Date)
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I hereby declare that all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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